

# PATENT SPECIFICATION

NO DRAWINGS

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**1,146,157**

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Int. Cl: —C 08 g 41/02, C 08 g 51/54

## COMPLETE SPECIFICATION

### Stabilized Polyamide Filaments

We, E. I. DU PONT DE NEMOURS & COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, 5 United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a process for preparing a stabilized filament of a synthetic linear polyamide, and is an improvement in, or modification of, the invention described 15 and claimed in U.K. Specification No. 902,906.

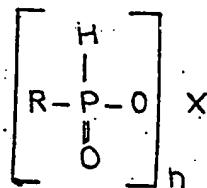
Polycarbonamide filaments, which are commercially known as nylon, can be stabilized against the action of heat by carrying out 20 the melt polymerization of the polymer in the presence of a minor amount of a phosphinate compound as a heat stabilizer. It is also known that nylons can be stabilized against the action of light by incorporating 25 into the polymer certain other salts as disclosed in U.K. Specification No. 793,132. The addition of salts, however, has in the past always been accompanied by undesirable results in the mechanical properties of 30 the yarn and the commercial processability of the yarn.

U.K. Specification No. 902,906 describes 35 and claims a process for preparing synthetic linear polycarbonamide filaments which comprises preparing the polymer by melt polymerization in the presence of a dissolved phosphinate compound of the formula

wherein R is a substituted or unsubstituted aliphatic alicyclic, aryl or aralkyl radical, X is an alkyl, aryl or aralkyl radical or a metal, or X and R together are an alkylene group forming a ring structure, incorporating into the polymer from 0.0002 to 0.050%, based on the weight of the polymer, of managanous hypophosphite, the dissolved phosphinate compound being employed in the melt polymerization in an amount of from 2 to 7 times the amount of the managanous hypophosphite, and thereafter extruding the molten polymer through an orifice to form a filament. 40

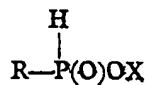
It is a main object of the present invention to provide a process for preparing a synthetic linear polycarbonamide filament stabilized against the action of both heat and light without an undesirable decrease in 45 yarn properties.

This invention provides a process of preparing a stabilized filament of a synthetic linear polycarbonamide, preferably polyhexamethylene adipamide, by melt polymerization in the presence of a dissolved phosphinate compound, other than a phosphinate compound for use in the process described and claimed in U.K. Specification No. 60 902,906, of the formula 65

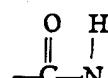


wherein

R is alkyl, cycloalkyl, alkenyl, aryl, aralkyl,



- or aralkenyl, and may be substituted with hydroxy, carboxy, carbalkoxy, cyano, amino, or halo radicals;
- 5      X is one of the radicals specified for R, an alkylene diammonium group, an alkyl substituted ammonium cation, or a metal; or X and R together are alkylene and form a ring structure; with the proviso that when X is a metal, n is a whole number corresponding to the valence of the metal, and when X is other than metal, n is one except that if X is an alkylene diammonium group, n is 2;
- 10     and incorporating into the polymer from 0.0002 to 0.050% by weight of the polymer of manganese hypophosphite, the said dissolved phosphinate compound being employed in the melt polymerization in an amount of from 2 to 7 times the amount of the manganese hypophosphite, and thereafter extruding the molten polymer through an orifice into a quenching medium to form a filament.
- 15     Thus the process of the present invention is to be construed as specifically excluding the process described and claimed in U.K. Specification No. 902,906.
- 20     Preferably the manganese hypophosphite is employed in amounts of from 0.003 to 0.025% by weight.
- 25     In a preferred embodiment the compound is employed in amounts of from about 3 to 6 times the amount of the manganese hypophosphite.
- 30     The stabilized filaments formed by the process of the present invention are included within the scope of this invention.
- 35     The term "synthetic linear polycarbonamide" means a conventional "nylon" polymer wherein the carbonamide linkages are an integral part of the main polymer chain. The expression "preparing the polymer by melt polymerization in the presence of a dissolved phosphinate compound" means that the phosphinate compound is present in the mixture of reactants during some part of the polymerization, i.e. they may be added before or during polymerization. The expression
- 40     "incorporating into the polymer" means that the manganese hypophosphite is added to the polymer prior to extrusion. The manganese hypophosphite, however, may be added to the reactants prior to polymerization so that it is present with the phosphinate compound at this stage or it may be added after polymerization is complete and the polymer is ready for extrusion.
- 45     The expression "extruding the molten polymer through an orifice into a quenching medium" is employed to mean the conventional melt-spinning process whereby the polymer is melted and forced through a hole or slot into a medium such as a liquid or
- 50     gas, generally air, or an inert gas, to cool and solidify the polymer into a long, substantially continuous structure. The use of plasticizers and other such means to facilitate extrusion and formation of filaments, particularly from high melting or somewhat unstable polymers is conventional and may be used in conjunction with this invention.
- 55     Among the suitable phosphinates for use in the process of this invention are barium phenylphosphinate, barium 2,5-dimethylphenylphosphinate, tetramethylammonium phenylphosphinate, and hexamethylene diammoniumphenylphosphinate.
- 60     The combination of the manganese hypophosphite and a phosphinate compound improves the stability of, and is particularly beneficial to, any synthetic linear polycarbonamide wherein the amide linkages are in the main polymer chain. Such polymers, in addition to containing a phosphinate and hypophosphite of this invention, may be modified by the addition of a moderate amount of antistatic and dyeing assistants such as polyvinylpyrrolidone and polyethylene oxide. The phosphinate compound should be added prior to heating the polyamide forming reactants to an elevated temperature near the melting point of the polyamide. It is essential that it be added prior to the melt-spinning operation. Conveniently, it may be added to the salt solution before the beginning of the polymerization reaction.
- 65     The manganese hypophosphite may be added during the polymerization or to the molten polymer prior to extrusion. In any event, it is necessary that it be present in the molten polymer as it is extruded if the unexpected processability of the present invention is to be obtained.
- 70     This invention particularly applies to linear polyamides whose carbonamide linkages are an integral part of the main polymer chain although some benefit may be obtained when using other synthetic linear fiber-forming nitrogen-containing condensation polymers (polycarbamides) such as polythioamides, polyureas, polythioureas, polyurethanes and polythiouethanes.
- 75     Typical of such polycarbonamides are those formed from an aliphatic diamine and an aliphatic acid containing the repeating unit
- 80     
$$\text{---X---Z---Y---Z---}$$
- 85     wherein X and Y represent divalent aliphatic, cycloaliphatic, or mixed aliphatic-cycloaliphatic groups, and ---Z--- represents the
- 90     linkage. Especially useful polyamides are those in which ---X--- and ---Y--- are  $(\text{CH}_2)_{n-1}$ , where n is a positive integer of
- 95     100     105     110     115     120

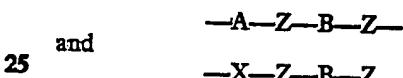


- from 1 to 12 inclusive. —X— and —Y— may be the same or different except that n cannot be 1 in both X and Y but only in one of them. Polyhexamethylene adipamide, 5 polycaproamide (i.e., "66" and "6" nylon) and polyundecanoamide are typical. Useful polyamides are also those in which —X— and/or —Y— is cycloaliphatic or aliphatic-cycloaliphatic, such as those derived from hexahydroterephthalic acid, bis(4-amino cyclohexyl)methane and bis(4-aminocyclohexyl)-propane-2.
- 10 Other suitable polyamides are those having the repeating structure



wherein —A— is a divalent aromatic radical and —X— and —Z— are as previously defined. Polyhexamethylene isophthalamide and poly(dimethyl hexamethylene terephthalamide) are illustrative of such polymers.

20 Additional polyamides having repeating units such as



30 where —B— is divalent alkaryl (such as xylylene) may be used provided that only the melt spinnable polymers and copolymers are intended. Poly(m-xylene adipamide) and poly(p-xylene sebacamide) are typical.

35 Another class of suitable polyamides containing other than aromatic intracarbonamide repeating units are those prepared from piperazine, such as those from piperazine and adipic acid, including methyl substituted derivatives of piperazine.

40 Melt-spinnable copolymers wherein the amide linkage is the predominant linkage, and mixtures of such copolymers may also be useful.

45 The stabilized polymeric compositions of this invention may also contain small amounts of such additives as antistatic agents, dyeing and coloring aids, and ultraviolet screens.

50 Polymers and copolymers stabilized according to this invention are useful for spinning continuous filaments, of round, lobed, and odd-cross section, and either of substantially uniform or of mixed deniers. These stabilized polymeric filaments may comprise core and sheath, side-by-side bicomponent, may be irradiation-grafted and may be of a hollow structure.

55 These stabilized polymeric filaments may be processed into tow and staple, and also may be bulked, crimped, textured, etc.

60 In a preferred embodiment of the present invention, a polymer is used which contains a small amount of a conventional delusterant such as titanium dioxide, barium sulfate, aluminum trioxide. Such materials and the

amounts employed are disclosed in U.S. Patent 2,205,722. At least 0.02%, and as much as 5% (by weight based on the weight of the polymer) of finely divided titanium dioxide is used for delustering purposes. Preferably, an amount of this delusterant is used within the range of from 0.02% to 2% (by weight based on the weight of the polymer).

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70 The process of the present invention may be carried out in a manner analogous to that more particularly described in Specification No. 902,906.

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75 The Applicants specifically disclaim the use in the process of the present invention of the phosphinate compounds disclosed in Specification No. 902,906.

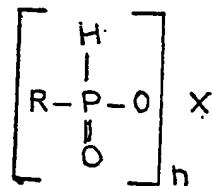
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80 Subject to the foregoing disclaimer, what we claim is:—

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1. A process for preparing a stabilized filament of a synthetic linear polycarbonamide by melt polymerization in the presence of a dissolved phosphinate compound of the formula

85



wherein

R is an alkyl, cycloalkyl, alkenyl, aryl, aralkyl, or alkenyl radical, and may be substituted with hydroxy, carboxy, carbalkoxy, cyano, amino or halo radicals;

90

X is one of the radicals specified for R, an alkylene diammonium group, an alkyl substituted ammonium cation, or a metal; or X and R together are alkylene and form a ring structure; with the proviso that when X is metal, n is a whole number corresponding to the valency of the metal, and when X is other than metal, n is one except that if X is an alkylene diammonium group, n is 2;

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and incorporating into the polymer from 0.0002 to 0.050%, by weight of the polymer, of manganous hypophosphite, the said dissolved phosphinate compound being employed in the melt polymerization in an amount of from 2 to 7 times the amount of the manganous hypophosphite, and thereafter extruding the molten polymer through an orifice into a quenching medium to form a filament.

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105 2. The process of claim 1 wherein the manganous hypophosphite is employed in an amount of from 0.003 to 0.025%.

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110 3. The process of claim 1 or 2 wherein the phosphinate compound is employed in

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- an amount of from 3 to 6 times the amount  
of the manganous hypophosphate.
4. The process of any one of claims 1 to 3  
wherein the phosphinate compound is any  
5 of those hereinbefore specifically mentioned.
5. The process of any one of claims 1 to  
4 wherein the polycarbonamide is polyhexa-  
methylene adipamide.
6. The process of claim 1, substantially as  
10 hereinbefore described.
7. A filament when produced by the pro-  
cess of any one of claims 1 to 6.

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